Synthesis and characterization of dandelion-like ZnO nanostructures

X. WANG[a*], Y. WANG[a], J. JIA[a], Y. TIAN[a], L. ZHANG[b,c]
[a]*Key Laboratory of Material Physics, and School of Physics and Engineering, Zhengzhou University, Zhengzhou 450052, P. R. China*
[b]*Postdoctoral research station of material science and engineering, zhengzhou university, Zhengzhou 450001, P. R. China*
[c]*Xinxiang University, Xinxiang 453002, P. R. China*

The dandelion-like ZnO nanostructures on silicon substrate were successfully synthesized by a simple thermal evaporation method using Zn and zinc acetate dihydrate as the source materials. Detailed structural characterizations confirm the single-crystalline with wurtzite hexagonal phase and exhibit that they are grown along the [0001] direction. Photoluminescence exhibits a weak UV emission at ~386 nm and a strong green emission at ~495 nm with 325 nm excitation. Field emission measurements demonstrate that the dandelion-like nanostructures possess good performance with a turn-on field of ~1.67 V/μm and a threshold field of ~7.22 V/μm.

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1. Introduction

Over the past few years, II–VI semiconductor nanomaterials have attracted extensive research interest because of their interesting optical, electrical and magnetic properties, and the possibility to fabricate nanodevices based on their unique properties. Among them, ZnO, a kind of semiconductor with direct bandgap (3.37eV) and large exciton binding energy (60meV), has attracted remarkable attention for a wide range of applications such as sensors [1,2], optoelectronics [3], solar cells [4] and field emission devices [5-7], due to its exciting electrical, optoelectronic and photochemical properties. It is well known that the size and morphology of nanomaterials have great effects on its properties and applications, then the control of shape and size is of great importance in order to fit different applications. Due to the polarity of ZnO crystal structure along the [0001] axis, the specific electrostatic interaction energy and chemical reactivity of O- and Zn- terminated polar surface enable the formation of an abundant family of ZnO nanoscale materials [8]. So far, all kinds of ZnO nanostructures, such as nanowires [9,10], nanorods [11,12], nanotetrapods [13], nanoplates [14], nanospheres [15], nanonails [16], nanoarrays [17-20], have been fabricated by different approaches, including thermal evaporation, hydrothermal synthesis, electrochemical deposition and template-based growth. However, such methods often use metal catalysts such as Au to assist and control the growth process, and the remains of metal particles at the tips of the ZnO nanostructures will influence their field emission properties and the purity of the final products.

In this paper, we report the synthesis of the novel dandelion-like ZnO nanostructures using a simple thermal evaporation method without the use of any metal catalyst. The optical, field emission properties are also investigated.

2. Experimental details

The dandelion-like ZnO nanostructures were synthesized on Si substrate by the thermal evaporation method without the use of any metal catalysts. The synthesis process was carried out in a horizontal quartz tube. Commercially available high purity metallic Zn powder (purity 99.999％), $Zn(CH_3COO)_2{\cdot}2H_2O$ (purity 99.00％) and oxygen gas (99.999%) were used as precursors of Zn and oxygen, respectively. Before being loaded, the Si (111) substrates were cleaned by acetone, etched by HF acid and washed with deionized water. Zn power (1g) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.2g) were loaded in the quartz boat. Then the quartz boat was placed in the middle of a quartz tube that was inserted in the horizontal tube furnace. The Si (111) substrate was loaded at the site of downstream gas flow, and the distance between the source and the substrate was about 12 cm. After evacuation of the quartz tube to about 0.2 Torr, a carrier gas of N_2 was introduced into the tube at a constant rate of 200 sccm, and then the furnace was heated to 500 ^oC. After reaching 500 ^oC, a nitrogen flow was lowered to 150 sccm, simultaneity O_2 was introduced with a constant flow of 50 sccm. Then the furnace was heated to 680 ^oC and maintained at this temperature for ~20 min (furnace pressure: ~650 Pa). During the cool down process, the flow of oxygen gas was closed, keeping the nitrogen gas flowing.

The as-synthesized ZnO nanostructures were characterized using the field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) pattern measured with Cu Kα radiation. The optical properties of the ZnO nanostructures were characterized by photoluminescence (PL) spectra at room temperature and the field emission (FE) characteristics were observed in a vacuum chamber at a pressure of 5×10^{-5} Pa.

3. Results and discussion

The crystallinity and orientation of the as-synthesized products grown on Si substrate was investigated by XRD, as shown in Fig. 1. The peaks are identified to originate from (100), (002), (101), (102), (110), (103) and (112) reflections of hexagonal ZnO crystal structure (a=0.325 nm, c=0.521 nm). The intensity of ZnO (002) peak is the highest one, which also suggests that the preferred growth orientation of the ZnO crystals is along the c-axis. Furthermore, no peaks for Zn or other impurities were detected in the spectrum, revealing the phase purity of the sample in the experimental error range.

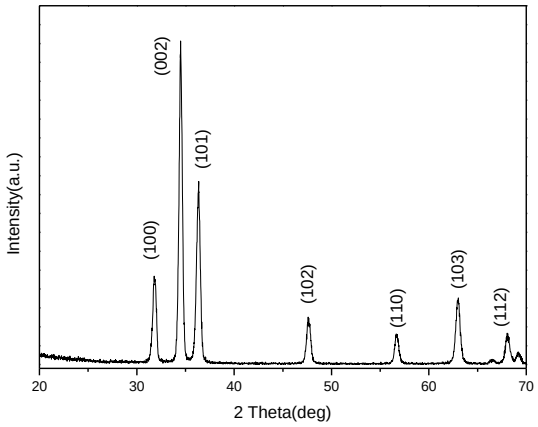

Fig. 1. XRD pattern of the dandelion-like ZnO nanostructures on Si substrate.

Fig. 2 shows the morphological and structural characterizations of the dandelion-like ZnO nanostructures. From Fig. 2(a), a large quantity of the dandelion-like ZnO nanostructures can be observed.

The magnified FESEM images shown in Fig. 2(b) and (c) indicate the detailed morphology of the dandelion-like ZnO nanostructures. Each individual dandelion consists of a well-faceted stem and the pompon. The diameter of the stem is about 20 nm, and the diameter of the pompon of the dandelion is about 200 nm.

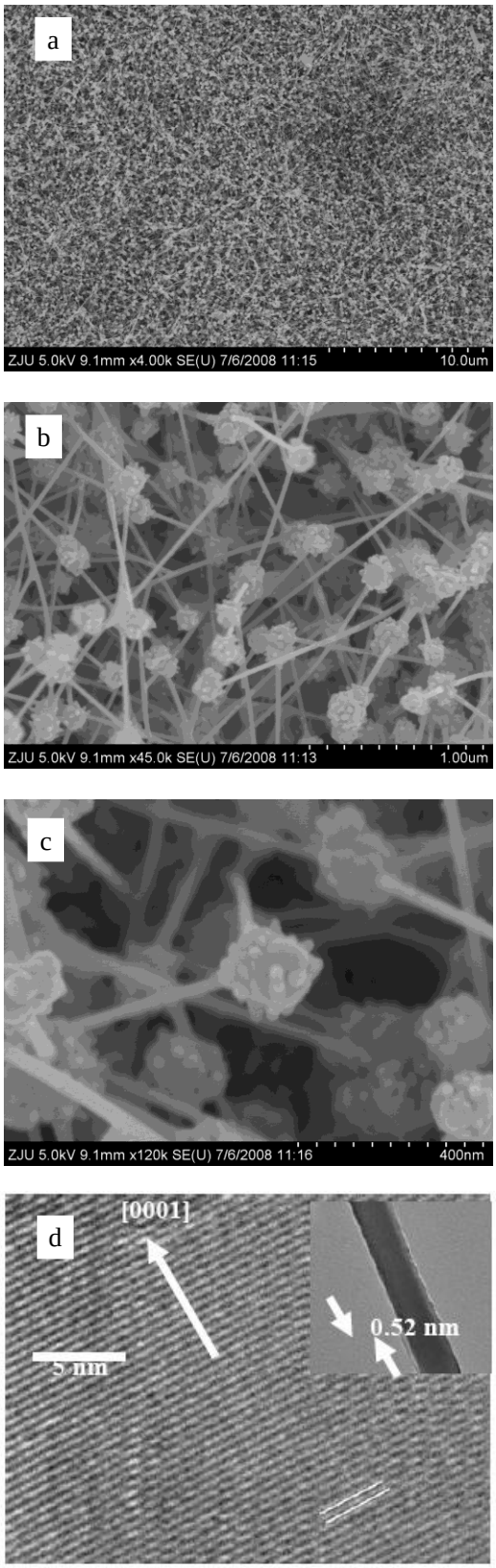

Fig. 2. (a) Low, (b) medium and (c) high magnification FESEM images of the dandelion-like ZnO nanostructures on Si substrate; (d) HRTEM image taken form the stem of the dandelion-like nanostructures, and the inset pattern is TEM image of the stem.

Furthermore, a minority of dumbbell-like nano structures composed of the stem and two pompons at stem ends is also observed as indicated in Fig. 2(b). Fig. 2(d) is HRTEM image taken from the stem of the dandelion-like nanostructures, and the inset pattern is a TEM image of the representative nanostructures. The HRTEM image shows the perfect lattice structure of the dandelion and confirms that the dandelion is a wurtzite type structure. The measured spacing of the lattice fringes is about 0.52 nm, which further confirms that the growth of the stem of the dandelion-like nanostructures is along the [0001] direction.

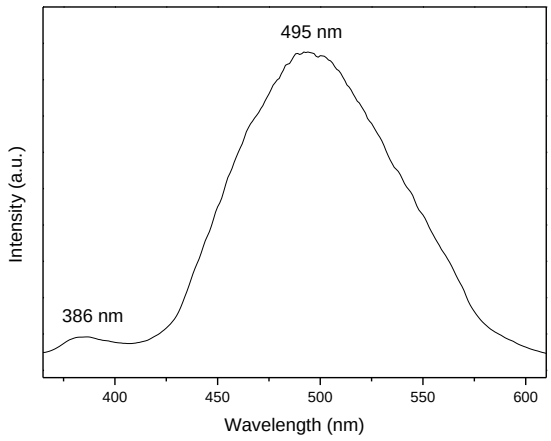

Fig. 3. Room temperature photoluminescence spectrum of the dandelion-like ZnO nanostructures on Si substrate.

It is well known that the densities of defects and oxygen vacancies affect significantly the physical properties of ZnO nanostructures. This correlation between structure and optical property was investigated by photoluminescence (PL) spectroscopy excited with the 325nm He-Cd laser. Fig. 3 shows that the room-temperature PL spectra of the as-grown ZnO products. From the PL spectra, two luminescence bands were seen: an ultraviolet (UV) near band-edge emission at ~386 nm and a green emission at ~495 nm. The UV emission can be explained by the band-edge emission resulting of the wide band gap ZnO from the recombination of free excitons through an exciton-exciton collision process [21]. The visible emission is usually considered to be associated with various intrinsic defects (oxygen vacancy, interstitial zinc and metal impurities) produced during ZnO preparation. It is generally accepted that the green emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy [22]. From Fig. 3, we observe that the visible emission is rather stronger than the UV emission, which indicates there may be more defects caused by the high temperature induced fast growth velocity. In addition, the low UV emission and the strong green emission from the dandelion-like ZnO nanostructures may also be attributed to the surface states being nonradiative centers due to their large surface-to-volume ratio [23]. These results show that the dandelion-like ZnO nanostructures with enhanced green light emission may be a promising material for application in optical nanodevices and related systems.

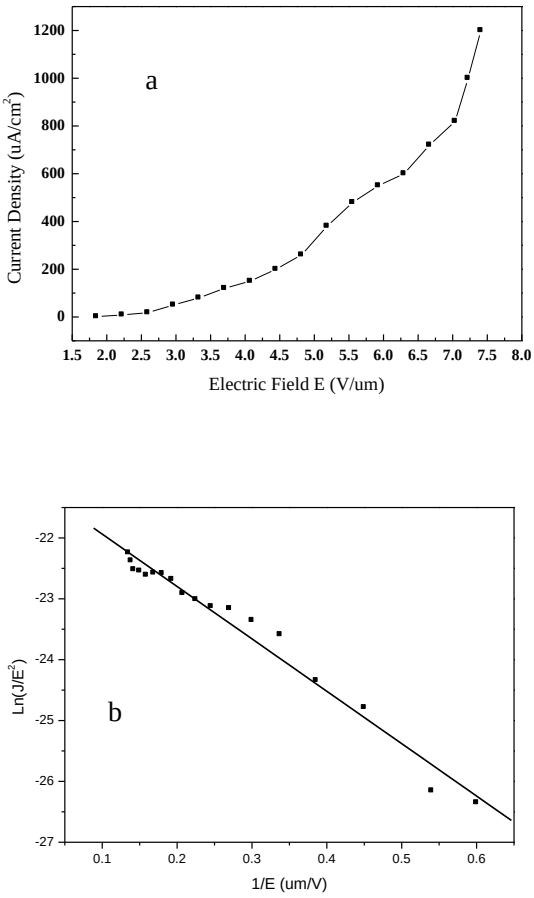

Fig. 4. Field emission properties of the dandelion-like ZnO nanostructures. (a) the J-E curve of the sample; (b) corresponding F-N plot showing linear dependence.

Besides its great interest for light-emitting devices, ZnO is also a good candidate for the FE application. The FE measurements were carried out in a vacuum chamber at a pressure of 5×10^{-5} Pa at room temperature. The sample with an area of 1 cm × 1 cm (as a cathode) was separated from a phosphor/ITO/glass anode by one isinglass spacer with the thickness of 270 μm. The emission current was measured under an applied voltage from 1 to 2500 V. Current versus voltage curves were measured with standard electronic instruments. In our experiment, the turn-on and threshold field are defined as the electrical field required producing a current density of 1 μA/cm^2 and 1 mA/cm^2, respectively. Fig. 4(a) depicts the typical curves of emission current density as a function of the applied electric field. As displayed in Fig. 4(a), the turn-on field of ~1.67 V/μm and threshold field of ~7.22 V/μm are obtained for the dandelion-like ZnO nanostructures. The FE properties are superior to those of the reported ZnO nanostructures with metal catalysts such as Au and Co [24-26] and catalyst-free ZnO nanostructures such as nanotubes [27], nanorods [6,28] and nanowires [29].

To further characterize the emission property of the dandelion-like ZnO nanostructures, the Frowler-Nordheim (F-N) law was employed to describe the exponential dependence between the emission current and the applied field. The F-N plot corresponding to the data in Fig. 4(a) is shown in Fig. 4(b). According to the F-N electron emission theory, the relationship between current density (J) and applied electric field (E) can be described as follows [30]:

$$J = A(\frac{\beta^2 E^2}{\Phi})\exp(\frac{-B\Phi^{3/2}}{\beta E}) \quad (1)$$

Where constant A is 1.54×10^{-6} A eVV^{-2} and constant B is 6.83×10^{9} eV$^{-3/2}$Vm^{-1}, β is the field enhancement factor, and φ is the work function which is estimated as 5.3 eV for ZnO [28]. The field enhancement factor β in the F-N plot shown in Fig. 4(b) can be calculated from the slope of the ln(J/E^2) versus (1/E) plot, and is estimated to be about 9681. Moreover, the F-N plot is found to be a good straight-line, indicating the cold field emission process from the ZnO nanostructures via quantum mechanical tunneling. These results suggest that the dandelion-like ZnO nanostructure is a promising material in future devices applications such as flat panel field emission displays.

4. Conclusions

Novel dandelion-like ZnO nanostructures have been fabricated at 680 ^{o}C on silicon substrate by the thermal evaporation method without the use of any metal catalyst. FESEM measurements show that each individual dandelion consists of a well-faceted stem and the pompon. Detailed structural characterizations confirm the single-crystalline with wurtzite hexagonal phase and exhibit that they are grown along the [0001] direction. The PL spectra of the obtained ZnO structures exhibit a weak UV emission at ~386 nm and a strong green emission at ~495 nm, showing good potential for the fabrication of optical nanodevices. Field emission measurements demonstrate that the dandelion-like nanostructures possess good performance with a turn-on field of ~1.67 V/μm and a threshold field of ~7.22 V/μm.

Acknowledgements

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* Corresponding author: wxclhm@zzu.edu.cn